Letters to the Editor

THIS section will accept reports of new work, provided these are terse and contain few figures, and especially few half-tone cuts. The Editorial Board will not hold itself responsible for opinions expressed by the correspondents. Contributions to this section should not exceed 600 words in length and must reach the office of the Managing Editor not later than the 15th of the month preceding that of the issue in which the letter is to appear. No proof will be sent to the authors. The usual publication charge ($8.00 per page) will not be made and no reprints will be furnished free.

The Structure of Cerium at the Temperature of Liquid Air*

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IN a dilatometric investigation of metallic cerium Trombe and Foex[1] observed under certain conditions a transition at 109°K which was accompanied by a 10 percent volume decrease and a decrease in magnetic susceptibility. Professor Linus Pauling suggested to us in 1946 that this transition is caused by the promotion of a 4*f* electron to a bond-forming orbital, and that the dense phase be studied by x-ray diffraction. The investigation described below was completed in 1948. Lawson and Tang[2] have recently produced the transition at 15,000 atmospheres; they found there essentially the same structure which we found at the temperature of liquid air.

Cerium containing 0.2 percent calcium, 0.2 percent magnesium, and 0.04 percent beryllium was supplied by Dr. F. H. Spedding. To obtain the low temperature transition we found it essential to remove the calcium and magnesium by melting in vacuum.[3] In an argon atmosphere 200-mesh filings from the remelted cerium were collected in thin-walled glass capillaries 0.3 mm in diameter. The capillaries were then sealed with or without evacuation, and were heat treated in a variety of ways including both quenching and slow cooling to room temperature from as high as 575°C. X-ray diffraction photographs were taken with *K* radiation from a molybdenum target filtered through zirconium. The specimen tube was mounted on the axis of a cylindrical camera. For low temperature photographs the sample was surrounded by a cellophane tube 3 mm in diameter; a continuous stream of liquid air kept the cellophane tube full and overflowed to wash the outside free of ice.

The face-centered cubic structure with $a_0 \approx 5.140$A explained all diffraction maxima observed from both quenched and annealed cerium at room temperature. We observed no lines which required a hexagonal closest-packed structure.

TABLE I. Diffraction maxima from quenched cerium at 90°K.

Line	Intensity	*d*	Normal phase *hkl*	Normal phase a_0	Dense phase *hkl*	Dense phase a_0
1	Str	2.760			111	4.780A
2	Str	2.400			200	4.800
3	Str Wide	1.813	220	5.128A		
4	Str Wide	1.703			220	4.817
5	Str Wide	1.549	311	5.137		
6	Str Wide	1.457			311	4.832
7	Wk Wide	1.396			222	4.836
8	Wk	1.106			331	4.821
9	Wk	1.077			420	4.816
10	Str Wide	0.986	511	5.123	422	4.830
11	M Wide	0.927			511	4.817
12	Str Wide	0.860	531	5.088		
13	Str Wide	0.812	620	5.135	531	4.803
14	V Wk Wide	0.772	622	5.121		
15	M Wide	0.673			{711 / 640}	{4.806 / 4.853}
16	V Wk	0.644			642	4.819
17	Wk	0.628			731	4.824

Only with cerium which had been quenched by an air blast from at least 300°C to room temperature could we obtain a transition at the temperature of liquid air. Data from a typical photograph are given in Table I.

The data show the presence in quenched cerium at 90°K of two phases. One is the normally contracted room-temperature form. The other is an anomalously contracted phase which is also face-centered cubic. Its cell edge of 4.82A represents a 16.5 percent decrease in volume below that of the parent structure.

The new dense form was produced several times. In successive coolings of a specimen with liquid air, a smaller and smaller proportion of the new structure appears. This effect has also been observed by Trombe. Apparently mechanical stresses must be present in the metal if the transition is to occur.

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[1] Felix Trombe and Marc Foex, Ann. d. chimie **19**, 417 (1944).
[2] A. W. Lawson and T. Y. Tang, Phys. Rev. **76**, 301 (1949).
[3] See Francoise Mahn, Comptes Rendus **223**, 78 (1946).

Rotational Isomerism in Substituted Ethanes

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THOMAS and Gwinn[1] have recently presented results on the configurations and relative energies of the rotational isomers in 1,1,2-trichloroethane and 1,1,2,2-tetrachloroethane derived from vapor phase dipole measurements. We wish to draw attention to the analogies and difference between these results and those obtained by us[2] from the study of the Raman spectra of the corresponding methyl derivatives of ethane (2-methylbutane and 2,3-dimethylbutane) in the liquid phase.

It was found that in both types of compounds the rotational isomeric composition remained approximately constant over a considerable temperature range, and further that in neither case could the 1,1,2,2 compounds consist solely of the centrosymmetric *trans*-isomer. The conclusions were all based on the observed qualitative behavior of the dipole moments and Raman spectra. The constant rotational isomeric composition was interpreted in both papers in terms of a very high or a very low energy difference between the rotational isomers. In the case of the chlorine compounds Thomas and Gwinn[1] concluded further from quantitative arguments that in 1,1,2,2-tetrachloroethane the energy difference is small (0 ± 200 cal. mole^{-1}) while in 1,1,2-trichloroethane it is large (>2300 cal. mole^{-1}). However, our tentative conclusion on the methyl derivatives was that the same explanation (of a high or a low energy difference) would apply to each hydrocarbon. As we stated before, accurate gas heat capacities would be well suited to choose between the alternative explanations.

Axford and Rank[3] have recently completed similar work on the infra-red spectra of the hydrocarbons in the liquid and solid states, and have confirmed our original conclusions. They find, moreover, that in the case of 2,3-dimethylbutane only one of the two strong, polarized Raman frequencies occurs in the infra-red spectrum in the 700–800 cm^{-1} region. This would be expected if one of these Raman lines was caused by the lowest skeletal stretching mode of the *trans*-molecule, but not if our alternative explanation of these two Raman lines in terms of Fermi resonance were correct. The combined infra-red and Raman results thus favor the presence of two rotational isomers with small energy difference in 2,3-dimethylbutane and, by analogy of the Raman spectra, very probably also in 2-methylbutane. In view of the conclusion of Thomas and Gwinn that steric rather than dipole repulsions are the more important factor determining the relative stabilities of the chloro-compound isomers also, 1,1,2-trichloroethane appears to be anomalous in having a large energy difference.